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Mid Infrared Water Quality Sensors for the Detection of Organic Pollutants

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Technical Report, Year 1

Research Activities September 01, 2002 – July 31, 2003

Boris Mizaikoff (PI)

Atlanta, September 28, 2003

1   TITLE:

MID-INFRARED WATER QUALITY SENSORS FOR THE DETECTION OF
ORGANIC POLLUTANTS

2   PROBLEM AND RESEARCH OBJECTIVE

Increasing pollution of water resources has stimulated the development of sensor systems capable of screening organic pollutants in the aquatic environment. Especially in urban areas, increasing concentration of volatile organic compounds in surface and ground water threaten primary sources of drinking water. Hence, there is a substantial demand for in-situ, continuously operating and reliable analysis methods emphasizing selective determination of abundant pollutants, such as chlorinated hydrocarbons (CHCs), pesticides or the broad class of endocrine disrupting compounds (EDCs).

The main goal of this research project is the optimization, application and validation of infrared chemical sensor systems for the determination of organic pollutants such as chlorinated hydrocarbons, pesticides or endocrine disrupting compounds in the Rottenwood Creek stream, an urban stream located in the metro Atlanta area. This stream is affected by residential, commercial and industrial land use. Synthetic sensing interfaces ('biomimetics') based on sol-gels and imprinted polymers emphasizing selective analyte recognition will be combined with existing infrared sensor systems already established by our research group. Following optimization of the instrument in the laboratory and validation with real-world samples, measurements at Rottenwood Creek are envisaged as representative example of an urbanized water resource.

3   METHODOLOGY

The methodology of this study is divided into three workpackages (**WPs**), which are described in the following sections:

• WP 1: Development of novel chemical recognition layers ("biomimetics") for optical waveguides based on sol-gels and molecularly imprinted polymers.

Sol-gel Chemistry

The sol-gel process represents a method of preparing glasses and ceramics at low temperatures by hydrolysis and polymerization of organic precursors and provides a promising platform for creating thin films at optical waveguide surfaces. Particularly, properties such as high chemical and mechanical stability and tunability of porosity and polarity make these materials attractive for sensing applications in harsh environments. By introducing organically modified siloxanes (Ormosils) as novel sol-gel precursors, reactive functional groups can be incorporated in the sol-gel matrix enabling the formation of improved chemical recognition elements. These chemical recognition elements are integrated with mid-infrared (mid-IR) waveguides serving both, as enrichment membrane and as protective layer. Two different kinds of IR transparent waveguides have been applied for developing intrinsic *evanescent field sensing systems*: ZnSe ATR crystals and silver halide fibers. Utilizing attenuated total reflection (ATR) techniques the environmentally relevant group of organophosphates has been targeted.

Molecularly Imprinted Polymers

Molecularly imprinted polymers are based on utilizing the functionalities of a target molecule (template) to assemble its own recognition cavity by forming interactions with 'complementary' functional groups of appropriate functional monomers. These interactions are either provided by cleavable covalent bonds or non-covalent interactions, which are then "frozen" in position by polymerization carried out in the presence of a high concentration of cross-linker. Subsequent removal of the template creates binding pockets within the polymer matrix memorizing the spatial arrangement of functional groups and the size and shape of the target molecule. Ideally, highly selective recognition of the imprinted analyte molecules is thereby ensured, which favors reversible re-binding and selective retention of the templated compound within the biomimetic recognition matrix.

First experiments have been performed to create highly selective separation materials for the endocrine disrupting compound (EDC) 17β-estradiol. HPLC columns packed with either molecularly imprinted stationary phase material or control (non-imprinted) material have been prepared and compared concerning their separation performance.

• WP 2: Optimization and testing of a fiber optic evanescent wave sensor prototype for measuring organic pollutants in the aquatic environment.

A prototype mid-infrared sensor system for the determination of volatile organic pollutants in ground and surface waters was developed and tested. The sensor comprises a portable Fourier transform infrared spectrometer, coupled to the sensor head via mid-infrared transparent silver halide fibre optic cables. A 10 cm unclad middle section of the 6 m long fibre is coated with ethylene propylene copolymer (E/PCo), in order to enrich the analytes within the penetration depth of the evanescent field protruding from the fibre sensor head. Alternatively, polymer coated ATR crystals are used. Mixtures of benzene, toluene and xylene isomers (BTX) at concentrations down to the low ppb region were successfully qualitatively and quantitatively investigated. All analytes could be simultaneously discriminated ; with LODs in the low ppb concentration range.

• WP 3: Alternative sensing concept for water analysis using an IR hollow waveguide gas sensing module combined with a supported capillary membrane sampler.

Following the proposed time schedule and work plan (see Figure 1) research was mainly focused on **WP 1** and **WP 2**.

4	PRINCIPLE FINDINGS AND SIGNIFICANCE

A major part of **WP 1** was dedicated to the development and investigation of organically modified sol-gel membranes as physico-chemical recognition element in chemical mid-IR evanescent field sensing systems [1,2]. In summary, following major parameters were studied: (i) influence of various organoalkoxysilanes on the membrane formation behavior for two different waveguides (planar ZnSe ATR crystals; silver halide optical fibers) and their resulting surface polarity, (ii) properties of sol-gel based membranes for water exclusion from the analytical volume probed by the evanescent field, (iii) response of the sensing system towards aromatic compounds containing nitro-functional groups with focus on the detection of organophosphate pesticides, (iv) characterization of the sensing system concerning response

time, sensitivity, reproducibility and stability, and (v) processing approaches enabling tunability of membrane porosity.

Due to significant IR absorption features of the sol-gel membranes below 1200 cm^{-1} the mid-IR fingerprint region (1200-600 cm^{-1}) is not accessible when applying sol-gel coated IR waveguides. Hence, during the first year of **WP 2** ethylene/propylene co-polymer coatings have been used to simultaneously quantify benzene, toluene and xylenes in water as these chlorinated hydrocarbons show molecule specific absorption features in the mid-IR fingerprint region [3].

Molecular imprinting procedures for the analyte 17β-estradiol have been developed and evaluated with the final goal of producing separation materials with improved selectivity for this specific analyte.

4.1 *Organically Modified Sol-Gel Membranes as Physico-Chemical Recognition Element in Mid-Infrared Evanescent Field Sensing Systems*

A Bruker IFS 66 research FT-IR spectrometers was used in the course of this work. The instrument was controlled via a desktop PC and equipped with a sample compartment for conventional ATR measurements and an external beam port for fiberoptic measurements. The mid-IR waveguides were coated with sol-gel membranes (1-10 μm thick) via spin- or drop-coating techniques and mounted into flow-through cells for analyte enrichment and detection studies. Exemplary sol-gel processing compositions for both, acid- and base-catalyzed approaches are presented in Table 1 and the common sol-gel processing procedures are described as follows:

Acid-catalyzed approach. The sol solution was prepared by acid-catalyzed co-polymerisation of a 3:1 mixture of PTMOS and TMOS in ethanol/water (molar ratio 4:3). 1.4 ml of PTMOS, 0.37 ml of TMOS, 1.5 ml of EtOH, 0.35 ml of H$_2$O and 0.5 ml of HCl (pH =1.7) were mixed, stirred at room temperature for 3 hours and aged overnight.

Base-catalyzed approach. In a typical synthesis 0.15 ml of CTAC (cetyltrimethylammonium chloride, 25 wt %) and 0.13 ml of 25 % aqueous NaOH solution were added to 2.5 ml of deionized water under stirring followed by addition of 0.127 ml of PTMOS. The vial was then sealed, stirred at room temperature for 2 hours and aged overnight.

4.1.1 Proof of Principle

Three organophosphates have been selected as target analytes for detection in an aqueous environment: parathion, fenitrothion and paraoxon (see Table 2). These compounds represent suitable test analytes due to their IR specific absorption features caused by the nitro-group. While IR spectra of pure organophosphates reveal a multitude of IR spectral features, the most noticeable mid-infrared spectral absorptions, when using sol-gel coated waveguides, are the asymmetric and symmetric stretching vibrations of the nitro group at 1522 cm^{-1} and 1347 cm^{-1} as these are located within the characteristic IR spectral window for sol-gel membranes. Besides, as depicted in Figure 2, the sensing system arrangement is capable of performing organophosphate detection in the lower ppm range.

4.1.2 Sensing Performance: Comparison of Sol-Gel Coated Waveguides to Conventional Polymer Coated Waveguides

Figure 3 shows a comparison of the sensor response after 60 min using an (a, c) uncoated, (b) Teflon AF, and (d) sol-gel coated ZnSE waveguide to 2.5 ppm and 40 ppm parathion,

respectively. It can be derived that neither the uncoated nor the Teflon coated waveguide are able to detect 2.5 ppm parathion with sufficient accuracy. A 40 ppm parathion solution measured with an uncoated crystal results in a clearly visible absorbance band, which shows approx. the same peak area as 2.5 ppm parathion detected with a sol-gel coated crystal. Hence, with respect to a bare ZnSe waveguide an enrichment factor of at least 20 is achieved in this example due to the sol-gel film. The fact that Teflon coated waveguides are not suitable for detection of these organophosphate analytes is probably related to the substantially higher hydrophobicity of Teflon. While Teflon is known to readily enrich chlorinated hydrocarbons, such as tricholoroethylene [4], sorption can be hindered in case of parathion by the polar character of the nitro-group. The additional advantage of sol-gel coated waveguides is that they require a significantly shorter sensor equilibration time in aqueous media (see Figure 4). Sol-gel membranes prepared from different organically modified precursors have also been analyzed in respect to their properties suppressing the water background. This feature is of particular importance for optical sensors based on mid-IR evanescent field spectroscopy as water is a strong IR absorber itself and would cause major interferences. The two graphs in Figure 5 demonstrate the ability of organically modified sol-gels to efficiently exclude water from the sensing region. The left part of the graph indicates that the surface polarity is not the only factor of influence in water suppression, otherwise the pure PTMOS coating should show the lowest water up-take. Membrane homogeneity and thickness certainly play an important role, which is demonstrated in the right graph, revealing that thicker coatings result in better water suppression. In the following, sol-gel membranes with thicknesses of about 1700 nm were used for further investigations. Although thicker films would additionally decrease interference by spectral water absorptions, thinner coatings were selected reducing the sorption time of the analyte and consequently providing shorter sensing response times.

4.1.3   Reproducibility

In order to investigate the reproducibility of the performed measurements with sol-gel coated sensing elements, repeated concentration series of two organophosphates, parathion and fenitrothion were analyzed. Results of three independent measurements of samples containing organophosphate concentrations between 0.5 ppm and 2.5 ppm are presented in Figure 6. The mean and standard deviation of repeated measurements at each enrichment time was determined and plotted vs. the input concentrations.

The results show that all peak area values fit a linear regression function and that the slopes of the linear fits increase with increasing enrichment times. These linear relationships were consistent for all measurement series as well as the fact that increased enrichment time corresponds to higher sensitivity. In particular, small error bars indicated in the right graph of Figure 6 demonstrate the reproducibility of this measurement technique. As the organophosphates reveal relatively long enrichment times into the sol-gel membranes different evaluation methods have been tested in respect to their applicability of analyzing the signal prior to the equilibrium state. Particularly, a chemometric approach using principle component regression (PCR) shows potential of evaluating the sorption curve before reaching the equilibrium, as already after 16 min the enrichment curve can be evaluated with similar accuracy to evaluation after 88 min. Improved algorithms currently developed in our laboratory will enable even faster evaluation of the sensor response.

4.1.4 Real World Measurements

In order to simulate real-world measurements, river water samples were collected from Peachtree Creek, an urban stream located in Atlanta, GA. Without any filtration or purification steps, the river water samples were spiked with 1 ppm and 10 ppm parathion, respectively. As a reference spectrum pure deionized water was used and a peristaltic pump assured a constant flow rate of 3 ml/min. In Figure 7 the response of a 1.7 μm acid catalyzed sol-gel coated ATR waveguide after 15 minutes is shown.

Both parathion concentrations are readily distinguished from the background signal indicating the feasibility of using sol-gel recognition layers for investigation of organophosphates at elevated concentration levels in a real-world aqueous environment.

As a concentration of 1 ppm is not a realistic environmental level for this type of pesticides the sensing system at the current development stage is not competitive with biosensors, which have limits of detection down to the sub μM (low ppb) concentration range [5]. However, as the sol-gel coated ATR system exhibits reliable performance and no degradation of the coating properties or optical behavior, it enables much longer operation times (up to several months) compared to biosensors. Strategies towards enhanced limits of detections for these optical sensing systems involve approaches aiming at improved control over porosity and hydrophobicity (see section 4.1.6).

4.1.5 Sol-Gel Coated Silver Halide Fiberoptic Waveguides

In the following, the use of silver halide fibers coated with porous sol-gels as mid-IR evanescent field sensing element for detection of nitro-based aromatic compounds is described. Due to the significantly lower costs of the chemical and lower toxic impact nitrobenzene was selected as model analyte in order to investigate potential and limitations of such sensing systems with respect to response behavior, reversibility of enrichment and reproducibility.

In order to ensure that the coating procedure provides a homogeneous film, scanning electron microscopy (SEM) images of the coated waveguide surface have been recorded and are presented in Figure 8. Derived from the SEM images and the known diameter of the fibers (700 μm) it can be estimated that the film thickness is in the range of 5 to10 μm for acid-catalyzed sol-gel membranes.

Results in Figure 9 demonstrate that nitrobenzene can be entirely removed after one enrichment process within 5 to 10 minutes of washing with the 10 % aqueous EtOH solution. Subsequent washing with water equilibrates the system for the next measurement. In the upper right corner of the left graph in Figure 9 desorption of the target analyte is shown applying only water during the regeneration step. The result clearly indicates that water extracts analytes slower from the sol-gel membrane due to the lower solubility of nitrobenzene in water compared to ethanol/water mixtures. Upon one hour of purging with water still a significant amount of nitrobenzene remains within the membrane. The left graph of Figure 9 also depicts the repeatability of the measurement procedure with a calculated RSD of 4.5 %. This value corresponds to similar ranges reported in literature (RSD of 2.5 % for poly(isobutylene)-coated sensor systems for reversible enrichment of tetrachloroethylene) [6]. Repeatability could be further improved by recording a new reference spectrum before each measurement. Herein reported experiments proof that no accumulation of analyte molecules ('memory effect') is evident within the sol-gel matrix even after several measurement cycles.

In order to further investigate reproducibility and to determine the limit of detection (LOD) of the applied method various concentrations of aqueous nitrobenzene solutions were prepared, pumped through the sensor flow cell and spectroscopically analyzed after an enrichment time of 10 min. The mean and standard deviation of repeated measurements in a concentration range of 40 ppm – 100 ppm were determined and plotted vs. input concentrations (see right graph of Figure 9). All peak height values fit a linear regression function with a correlation coefficient of 0.9951. The LOD for nitrobenzene is 10 ppm, which corresponds to a signal 3 times higher than the standard deviation of the background noise. Longer enrichment times result in lower LODs, e.g. sorption times of 60 min improve the LOD by a factor of approximately 2.

4.1.6 Approach to Influence Porosity of Thin Sol-Gel Membranes

So far, only acid-catalyzed sol-gel recognition layers have been reported for mid-IR applications [7] as usually crack-free thin films are obtained. However, as sol-gel materials are tunable in pore size distribution and porosity depending on the choice of catalyst, it is of great interest to compare acid- and base-catalyzed sol-gel layers with respect to their enrichment behavior.

Figure 10 depicts the comparison of enrichment properties of HCl- and NaOH-catalyzed sol-gels when exposed to aqueous parathion solutions in the lower ppm concentration range. The left graph shows data obtained with AgX fibers and results for ZnSe crystals as waveguides are shown in the right graph. The base-catalyzed material yields significantly better enrichment and faster penetration into the sol-gel membrane reaching the t_{90} value (90 % of enrichment) after approximately 40 min (AgX fibers) and after approximately 120 min (ZnSe crystals), respectively, while in case of the acid-catalyzed type the sorption process does not reach equilibrium even after 120 min of enrichment time. This effect is consistent with larger pores and higher porosity of base-catalyzed sol-gel materials reported in literature [8]. Furthermore, collapse and shrinkage of the pore channels during the drying process is usually less pronounced than for the acid catalyzed sol-gels, which would enhance access for the analyte parathion.

4.1.7 Summary

Thin film membranes with a thickness of a few μm have been fabricated at the surface of planar ATR crystals and silver halide fibers using mixtures of the precursor tetramethoxysilane (TMOS) and low molecular weight organoalkoxysilanes with various functionalities. The 3:1 molar mixture of phenyltrimethoxysilane and tetramethoxysilane yields films of high homogeneity with comparatively hydrophobic properties confirmed by water contact angle measurements. This approach results in excellent water suppression, which is a prerequisite for successful IR measurements in aqueous environments. The organophoshates parathion, fenitrothion and paraoxon were detected in the low ppm and sub-ppm concentration range using acid-catalyzed sol-gel films. High stability and reproducibility was demonstrated, however, contrasted by enrichment times of several hours. Hence, a variety of kinetic signal evaluation methods were investigated to minimize the response time of the sensing system. Multivariate concentration evaluation methods based on multivariate linear regression and principle component regression proved advantageous over conventional linear regression models enabling reliable signal evaluation after approx. 30 min. Real world measurements of parathion spiked river water samples indicated the feasibility of such an *in situ* sol-gel based chemical IR sensing system especially for field screening applications which are not sensitive to the response time and for expected concentration ranges in the sub-ppm region. For the first time the combination of sol-gel based membranes with mid-IR transparent silver halide fibers was demonstrated, which is

particularly important as such robust sol-gel materials significantly improve the lifetime of these delicate fiber materials. In addition, evanescent field spectroscopy enables *in situ* monitoring of the sol-gel coating, drying and aging process. Reversible enrichment of nitrobenzene for multiple measurement cycles was shown and linear relationship between peak height of selected absorption bands and input concentrations was obtained. When comparing acid- and base-catalyzed sol-gel membranes faster response time and enhanced enrichment are yielded for the environmentally relevant pesticide parathion, which corroborates the theory of larger pores and higher porosity for base-catalyzed sol-gels.

4.2 *Simultaneous Quantitative Determination of Benzene, Toluene and Xylenes in Water Using Mid-Infrared Evanescent Field Spectroscopy*

Attenuated total reflection mid-infrared (ATR-IR) spectroscopy using ZnSe ATR crystals is applied for simultaneous detection and quantification of the environmentally relevant analytes benzene, toluene, and the three xylene isomers (BTX). The analytes are enriched into a thin ethylene/propylene co-polymer membrane coated onto the surface of the internal reflection waveguide, which is exposed to the aqueous sample. As shown in Figure 11 linear relationships between characteristic absorption peak areas vs. input concentrations with R^2-values > 0.99 have been obtained for each analyte along with high reproducibility for 5 consecutive measurements. Detection limits lower than 20 ppb (v/v) have been achieved for all xylene isomers and of approx. 80 ppb (v/v) for benzene and 50 ppb (v/v) for toluene, respectively. Equilibrium conditions for this diffusion based sensor were achieved within approx. 18 min. At the present stage of development the sensor system is suitable as analytical device for online, in-situ process monitoring of multiple organic components at low ppb concentrations.

4.3 *Molecularly Imprinted Polymers Selective For β-Estradiol*

Experimental. The polymers were prepared using bulk polymerization by initially dissolving the template molecule 17β-estradiol in a mixed solvent (9 ml acetonitrile with 3 ml acetone). Upon the successive addition of the functional monomer (MAA), the cross-linker (EDMA), and the initiator (0.381 mmol) the reaction mixture was degassed by sonication and saturated with argon for 5 min. Afterwards, the tubes were sealed under argon and the pre-polymerization mixture were thermally polymerized at 60 °C for 16 h. Subsequently, the bulk polymers were dried at 40 °C in an oven and each polymer was ground with a mechanical mortar and sieved in acetone to yield a fraction with a particle size < 25 μm. Fine particles were removed by repeated sedimentation in acetone. The polymer particles were slurry-packed into a stainless steel HPLC column (250×4.6 mm) and the template was extracted by washing with methanol-acetic acid (85:15, v/v) for 6 h. The control polymer was prepared in exactly the same way without adding the template molecule.

Results. The results of the chromatographic separation of 17α-estradiol and 17β-estradiol using imprinted polymer and control polymer as stationary HPLC phases are presented in Figure 12. While HPLC runs using control polymers as stationary phase did not result in a separation of these structurally very similar analytes, separation can be achieved when applying imprinted polymers as stationary phase. These results indicate the existence of 17β-estradiol selective recognition sites and can be seen as a first step towards the formation of highly selective separation materials for the endocrine disrupting compound (EDC) 17β-estradiol.

5 WORKING PLAN FOR THE 2nd Year

- ➢ Continued development of sol-gel chemistry towards better control on porosity and surface termination for increased sensitivity.

- ➢ Continued MIP development for (i) sensing applications and (ii) suspension polymerization strategies for the development of MIP beads for SPE and HPLC applications.

- ➢ Collaboration with USGS Atlanta to coordinate real-world measurements at Rottenwood Creek with accompanying validation.

- ➢ Field measurements at Rottenwood Creek.

- ➢ Prototype IR evanescent field sensor for in-situ chlorinated hydrocarbon analysis.

- ➢ Hollow waveguide based IR sensor for VOC analysis.

6 FIGURES AND TABLES

	1ST YEAR (QUARTERS)				2ND YEAR (QUARTERS)			
	1	*2*	*3*	*4*	*1*	*2*	*3*	*4*
WP 1	Development of chemical recognition layers based on sol-gels							
			Implementation of sol-gels as coating materials for the fiber optic evanescent wave sensor system					
	Molecular imprinting strategies for selected organic pollutants							
			Characterization of molecularly imprinted polymers and their application as novel recognition layers					
WP 2	Optimization of the FT-IR based fiber optic evanescent wave sensor prototype							
	Measurement of real-world samples							
					Field measurements at Rottenwood Creek			
WP 3			Alternative sensing concept based on IR hollow waveguide sensor combined with capillary membrane sampler					

Figure 1: Time schedule and work plan
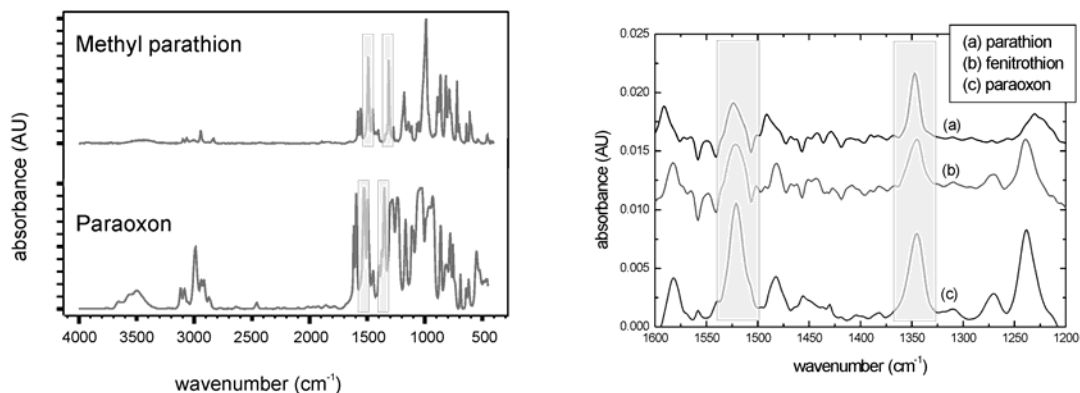
Figure 2: (left) Pure IR spectra of methyl parathion and paraoxon obtained from the Bio-Rad Sadtler IR database, (right) ATR spectra of 2.5 ppm parathion, 2.5 ppm fenitrothion, and 3 ppm paraoxon, 1.7 μm acid catalyzed PTMOS/TMOS sol-gel coated ZnSe ATR crystal, gray areas indicate the wavenumber region suitable for concentration evaluation by peak area integration.
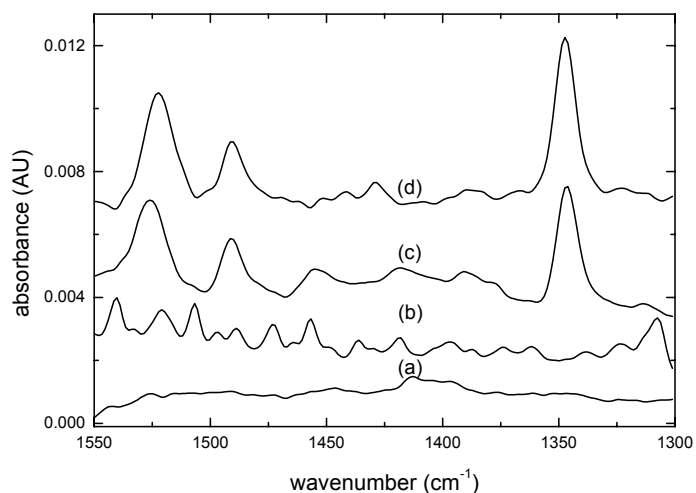

Figure 3: Response to the organophosphate parathion produced after 60 minutes by ZnSe waveguide sensors mounted in a flow-through cell. Spectra are shifted in the y axis for better illustration. (a) uncoated waveguide purged with 2.5 ppm parathion (b) an Teflon AF coated waveguide purged with 2.5 ppm parathion (c) uncoated waveguide purged with 40 ppm parathion (d) sol-gel coated waveguide purged with 2.5 ppm parathion.
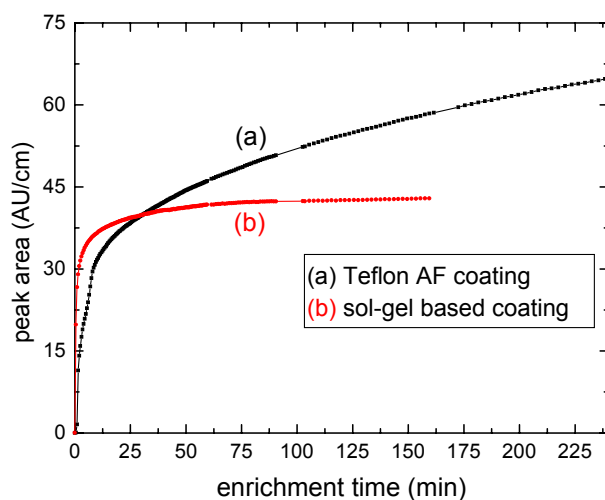
Figure 4: Comparison of water up-take of coatings based on Teflon AF (3 μm thick) and PTMOS/TMOS sol-gels (2 μm thick) on ZnSe crystals, monitored via ATR FT-IR spectroscopy.
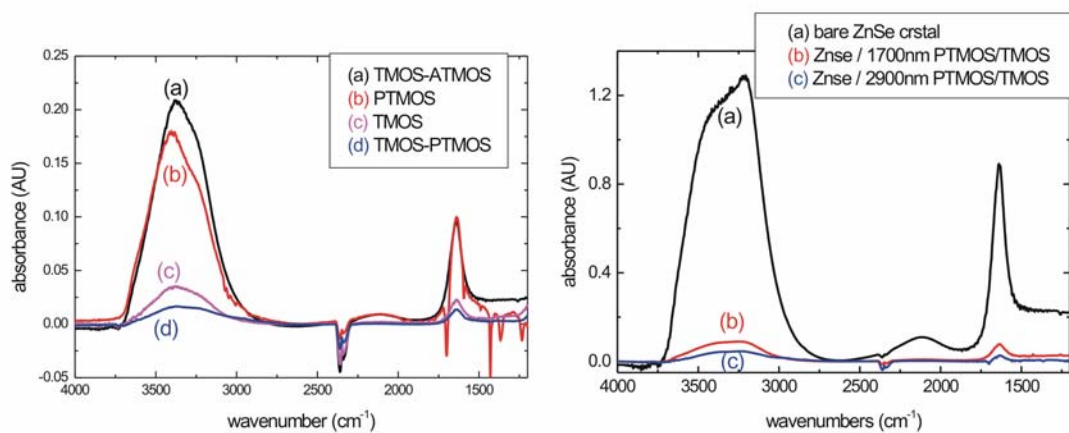
Figure 5: IR absorption caused by water up-take of sol-gel membranes on ATR crystals: (right) influence of various sol-gel precursors on the water suppression, (left) comparison of the water spectrum recorded using a bare crystal with sol-gel coated ATR elements of different membrane thicknesses.
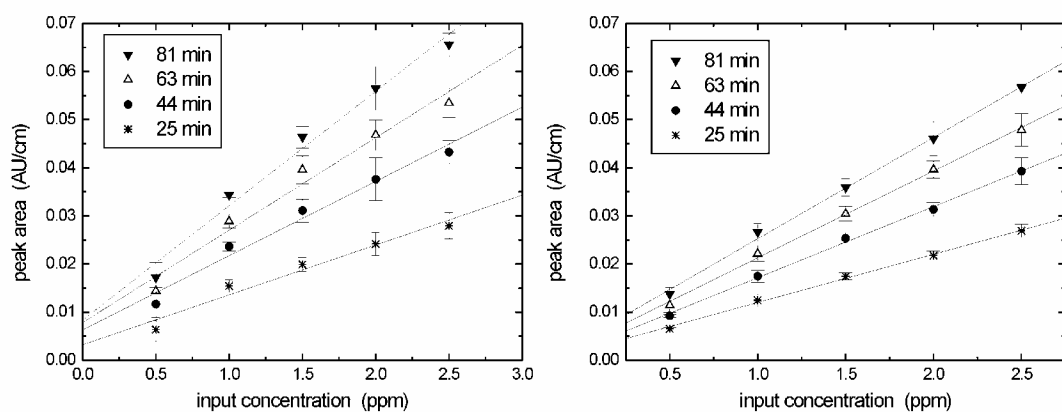
Figure 6: Calibration curve of fenitrothion (left) and parathion (right) over the concentration range of 0.5 – 2.5 ppm evaluated at different times during the enrichment process (error bar on the highest concentration point of the 81 minute data point for parathion is missing due to only two available data points).
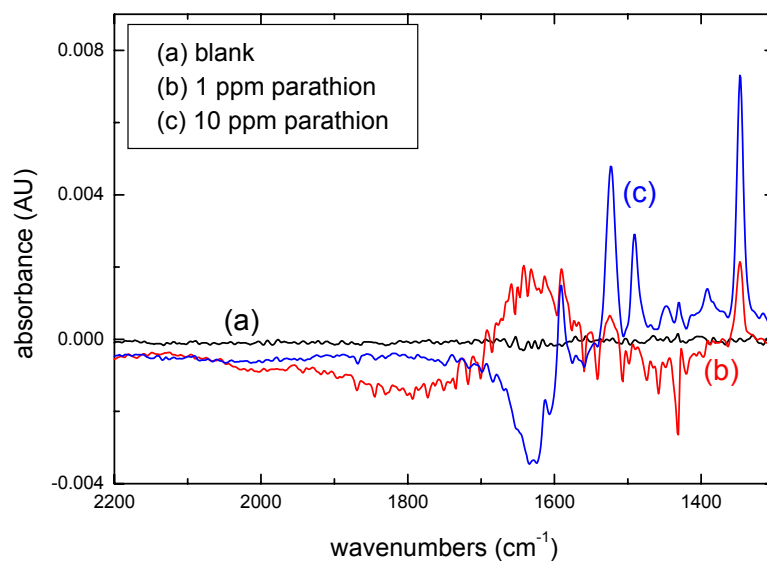
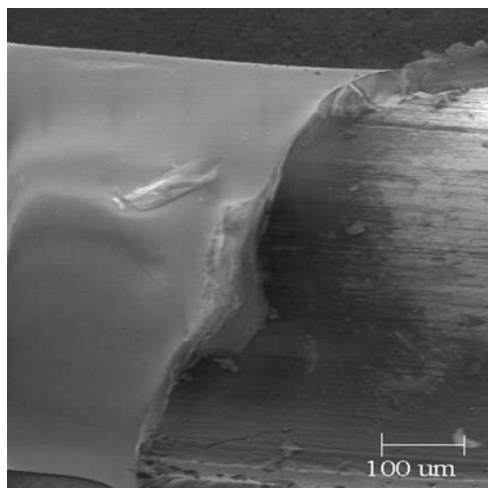Figure 7: Sensor response after 15 minutes to 1 ppm and 10 ppm parathion spiked river water.

Figure 8: SEM images of sol-gel coated silver halide fibers. The right section of each fiber was protected with tape before application of the sol-gel coating.
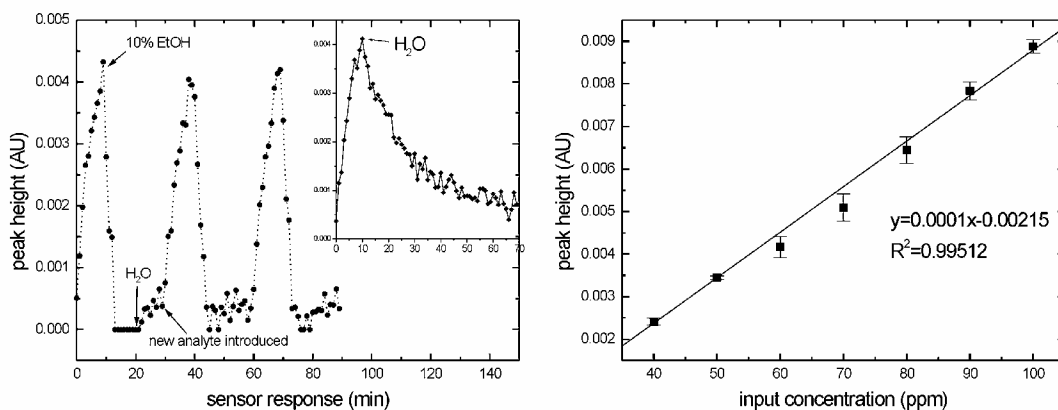
Figure 9: (left): Enrichment and desorption of a 50 ppm nitrobenzene solution using acid-catalyzed sol-gel coating, (right): Calibration curve of nitrobenzene over the concentration range of 40 – 100 ppm using acid-catalyzed sol-gel coating and performing three consecutive measurements.
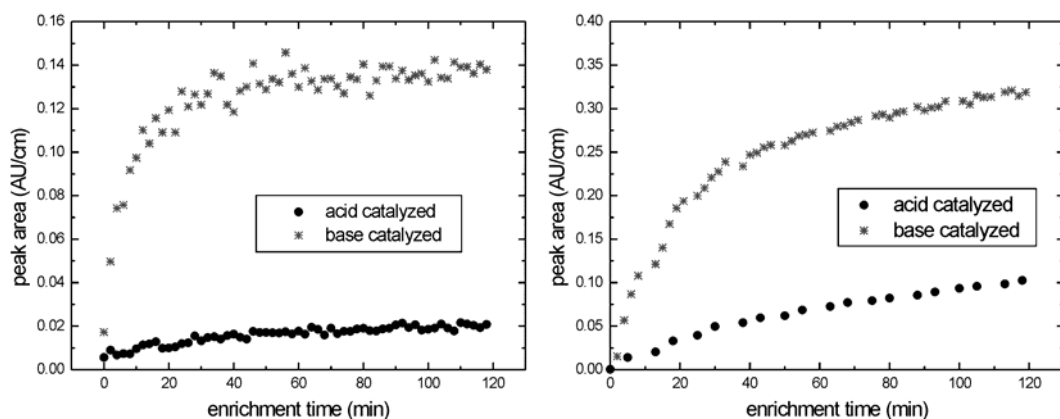
Figure 10: Comparison of enrichment behavior of acid- and base-catalyzed sol-gels, (left) using AgX fibers and a 50 ppm parathion solution; (right) using ZnSe crystals and a 2.5 ppm parathion solution.
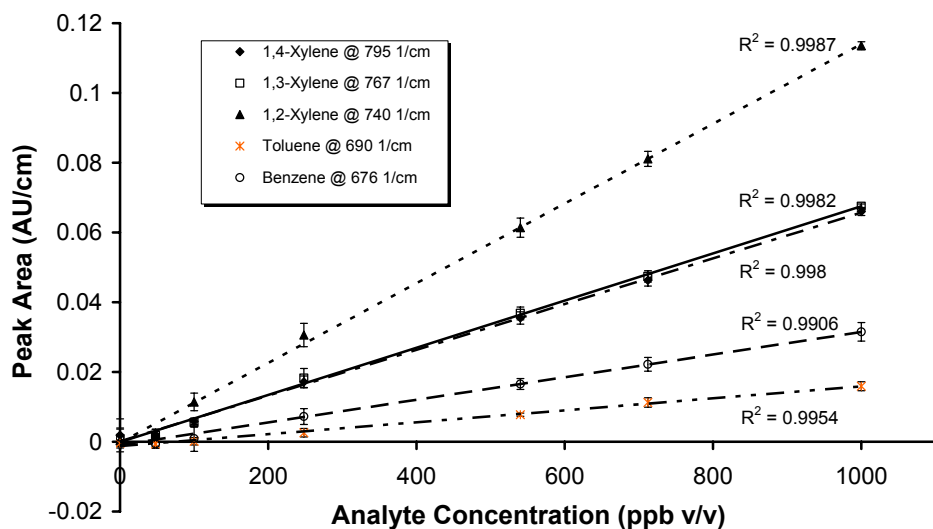

Figure 11: Calibration graphs for benzene, toluene and the xylene isomers in the concentration range of 0 – 1000 ppb (v/v) based on peak area integration. The error bars represent the standard deviation of five subsequent measurements.
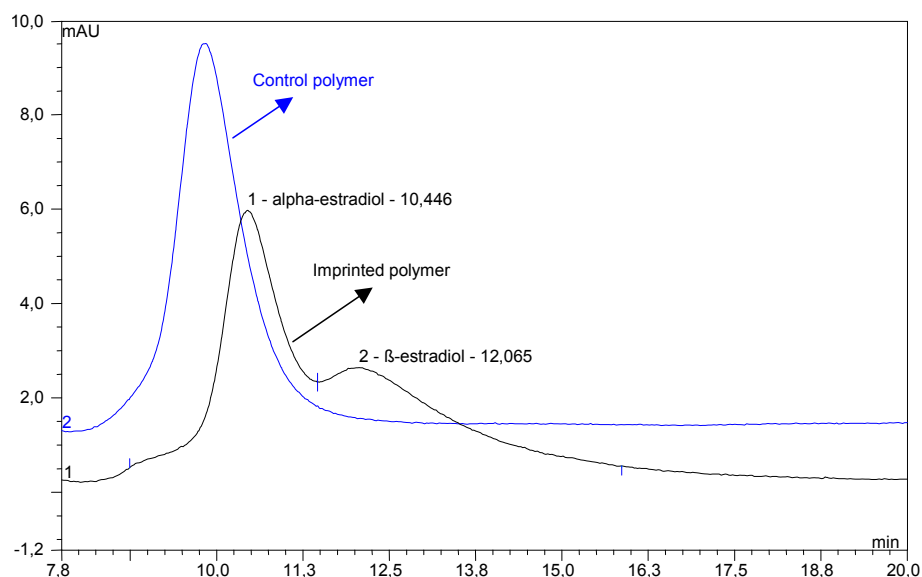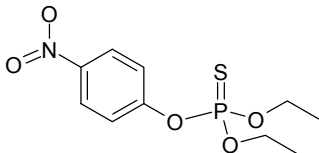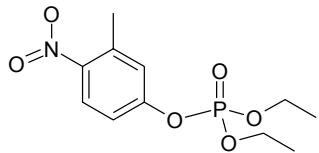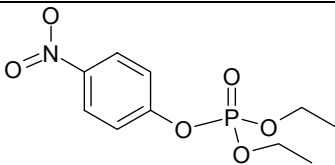
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Figure 12: Chromatographic separation of 17α-estradiol and 17β-estradiol (1×10^{-2} µg each) using imprinted polymer, and control polymer as stationary phase. 250×4.6 mm stainless steel columns were used. Acetonitrile containing 1% acetic acid was applied as mobile phase at a flow rate of 0.6 ml/min.

Table 1: Composition of pre-polymerization sol-gel mixture for acid and base catalyzed approaches.

		acid catalyzed (ml)	base catalyzed (ml)
sol-gel precursor	PTMOS	1.4	0.127
	TMOS	0.37	
catalyst	HCl	0.5	
	25% NaOH		0.065
	H_2O	0.35	2.5
solvent	EtOH	1.5	
surfactant	cetyltrimethyl-ammonium chloride		0.15

Table 2: *Selected organophosphates including their chemical structure and properties*

	Chemical structure	Comments
Parathion		rapidly hydrolyses at alkaline conditions (pH>10); hydrolytically stable under sterile conditions at pH 4 – 9; very toxic to aquatic organisms; may cause long-term effects in the aquatic environment; classified as a Restricted Use Pesticide (RUP)
Fenitrothion		less toxic than parathion; heavily used in countries, such as Japan where parathion has been banned
Paraoxon		active metabolite of parathion; inhibits cholinesterase and is further metabolized to compounds, such as para-nitrophenol

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